

What is claimed is:

1. A processing solution for forming a hexavalent chromium free, corrosion resistant trivalent chromate conversion film on zinc or zinc alloy plating layers, which comprises:

5 trivalent chromium and oxalic acid in a molar ratio ranging from 0.5/1 to 1.5/1, wherein the trivalent chromium is present in the form of a water-soluble complex with oxalic acid; and

 cobalt ions, which are stably present in the processing solution without causing any precipitation due to formation of a hardly soluble metal salt with oxalic acid;

10 wherein the solution reacts with zinc when bringing it into contact with the zinc or zinc alloy plating to form a hexavalent chromium free, corrosion resistant, trivalent chromate conversion film containing zinc, trivalent chromium, cobalt and oxalic acid on the plating.

15 2. The processing solution according to claim 1 wherein molar ratio of trivalent chromium to oxalic acid ranges from 0.8/1 to 1.3/1.

3. The processing solution according to claim 1 wherein the trivalent chromium concentration ranges from 0.2 to 5 g/L, the oxalic acid concentration ranges from 0.2 to 13 g/L and the cobalt ion concentration
20 ranges from 0.2 to 10 g/L.

4. The processing solution according to claim 1 wherein the trivalent chromium concentration ranges from 1 to 5 g/L, the oxalic acid concentration ranges from 2 to 11 g/L and the cobalt ion concentration ranges from 0.5 to 8 g/L.

25 5. The processing solution according to claim 1 which further comprises 1 to 50 g/L of an inorganic salt selected from the group consisting of inorganic salts of nitric acid, sulfuric acid and hydrochloric acid.

6. The processing solution according to claim 1 wherein pH ranges from

0.5 to 4.

7. The processing solution according to claim 1 wherein molar ratio of trivalent chromium to oxalic acid ranges from 0.8/1 to 1.3/1;

the trivalent chromium concentration ranges from 1 to 5 g/L, the oxalic acid concentration ranges from 2 to 11 g/L and the cobalt ion concentration ranges from 0.5 to 8 g/L;

it further comprises 1 to 50 g/L of an inorganic salt selected from the group consisting of inorganic salts of nitric acid, sulfuric acid and hydrochloric acid; pH ranges from 0.5 to 4.

8. A hexavalent chromium free, corrosion resistant, trivalent chromate conversion film containing zinc, trivalent chromium, cobalt and oxalic acid and formed on zinc or zinc alloy plating layers, wherein the mass ratio of trivalent chromium to (trivalent chromium + zinc) $[Cr/(Cr + Zn)]$ is not less than 15/100, the mass ratio of cobalt to (trivalent chromium + cobalt) $[Co/(Cr + Co)]$ ranges from 5/100 to 40/100 and the mass ratio of the oxalic acid to (trivalent chromium + oxalic acid) $[oxalic\ acid/(Cr + oxalic\ acid)]$ ranges from 5/100 to 50/100.

9. A hexavalent chromium free, corrosion resistant, trivalent chromate conversion film containing zinc, trivalent chromium, cobalt and oxalic acid and formed on zinc or zinc alloy plating layers, wherein the mass ratio of trivalent chromium to (trivalent chromium + zinc) $[Cr/(Cr + Zn)]$ is not less than 20/100 to 60/100, the mass ratio of cobalt to (trivalent chromium + cobalt) $[Co/(Cr + Co)]$ ranges from 10/100 to 40/100 and the mass ratio of the oxalic acid to (trivalent chromium + oxalic acid) $[oxalic\ acid/(Cr + oxalic\ acid)]$ ranges from 10/100 to 50/100.

10. The film according to claim 9 wherein the thickness of the film is not less than $0.02\ \mu m$.

11. A method for forming a hexavalent chromium free, corrosion resistant,

trivalent chromate conversion film comprising:

the step of bringing zinc or zinc alloy plating layers into contact with a processing solution comprising trivalent chromium and oxalic acid in a molar ratio ranging from 0.5/1 to 1.5/1, wherein the trivalent chromium is present in the form of a water-soluble complex with oxalic acid, and cobalt ions, which are stably present in the processing solution without causing any precipitation due to formation a hardly soluble metal salt with oxalic acid; wherein the solution reacts with zinc to form a hexavalent chromium free, corrosion resistant, trivalent chromate conversion film containing zinc, trivalent chromium, cobalt and oxalic acid on the plating.

12. The method according to claim 11 wherein, in the processing solution, molar ratio of trivalent chromium to oxalic acid ranges from 0.8/1 to 1.3/1.

13. The method according to claim 11 wherein, in the processing solution, the trivalent chromium concentration ranges from 0.2 to 5 g/L, the oxalic acid concentration ranges from 0.2 to 13 g/L and the cobalt ion concentration ranges from 0.2 to 10 g/L.

14. The method according to claim 11 wherein the processing solution further comprises 1 to 50 g/L of an inorganic salt selected from the group consisting of inorganic salts of nitric acid, sulfuric acid and hydrochloric acid.

15. The method according to claim 11 wherein the processing solution has pH of 0.5 to 4.

16. The method according to claim 11 wherein, in the processing solution, molar ratio of trivalent chromium to oxalic acid ranges from 0.8/1 to 1.3/1; the trivalent chromium concentration ranges from 0.2 to 5 g/L, the oxalic acid concentration ranges from 0.2 to 13 g/L and the cobalt ion concentration ranges from 0.2 to 10 g/L;

the processing solution further comprises 1 to 50 g/L of an inorganic salt selected from the group consisting of inorganic salts of nitric acid, sulfuric

acid and hydrochloric acid;

pH ranges from 0.5 to 4.

17. The method according to claim 11 wherein the step of contacting is conducted at a temperature of the solution of 10 to 40 °C for 5 to 600
5 seconds.

18. A method for forming a hexavalent chromium free, corrosion resistant, trivalent chromate conversion film comprising the steps of:

immersing zinc or zinc alloy plating layers into a dilute nitric acid solution and then water rinsing;

10 subjecting the zinc or zinc alloy plating layers to immersion in a processing solution and then water rinsing, wherein the processing solution comprises trivalent chromium and oxalic acid in a molar ratio ranging from 0.5/1 to 1.5/1, wherein the trivalent chromium is present in the form of a water-soluble complex with oxalic acid, and cobalt ions, which are stably present in
15 the processing solution without causing any precipitation due to formation of a hardly soluble metal salt with oxalic acid; and drying the resultant;

wherein the solution reacts with zinc to form a hexavalent chromium free, corrosion resistance, trivalent chromate film containing zinc, trivalent
20 chromium, cobalt and oxalic acid on the plating.

19. The method according to claim 18 wherein, in the processing solution, molar ratio of trivalent chromium to oxalic acid ranges from 0.8/1 to 1.3/1; the trivalent chromium concentration ranges from 0.2 to 5 g/L, the oxalic acid concentration ranges from 0.2 to 13 g/L and the cobalt ion concentration
25 ranges from 0.2 to 10 g/L;

the processing solution further comprises 1 to 50 g/L of an inorganic salt selected from the group consisting of inorganic salts of nitric acid, sulfuric acid and hydrochloric acid;

pH ranges from 0.5 to 4.

20. The method according to claim 18 wherein the step of immersing is conducted at a temperature of the solution of 10 to 40 °C for 5 to 600 seconds.

5 21. The method according to claim 18 wherein the step of immersing is conducted at a temperature of the solution of 20 to 30 °C for 20 to 60 seconds.

22. The method according to claim 18 wherein the step of immersing is conducted at a temperature of the solution of 10 to 40 °C for 5 to 600 seconds
10 and the step of drying is conducted at a temperature of 60 to 80 for 10 minutes.

23. The method according to claim 18 wherein, before or after the step of drying, further a topcoat film is applied onto the hexavalent chromium free, corrosion resistant, trivalent chromate conversion film.

15 24. The method according to claim 18 which, before or after the step of drying, further comprises applying an topcoat film onto the hexavalent chromium free, corrosion resistant, trivalent chromate conversion film by immersing the film in a topcoating solution comprising one member selected from the group consisting of a silicate or a phosphoric acid salt, polyethylene,
20 polyvinyl chloride, polystyrene, polypropylene, methacrylic resin, polycarbonate, polyamide, polyacetal, fluorine plastic, urea resin, phenolic resin, unsaturated polyester resin, polyurethane, alkyd resin, epoxy resin and melamine resin.

25 25. The method according to claim 24 wherein the topcoating solution comprises one member selected from the group consisting of a silicate acid salt, methacrylic resin and polyurethane.

26. A method for forming a colored hexavalent chromium free, corrosion resistant, trivalent chromate conversion film comprising:

the step of bringing zinc or zinc alloy plating layers into contact with the processing solution of claim 1 further containing a dye, or the steps of bringing zinc or zinc alloy plating layers into contact with the processing solution of claim 1 and then applying to the resultant a solution containing a dye.

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